

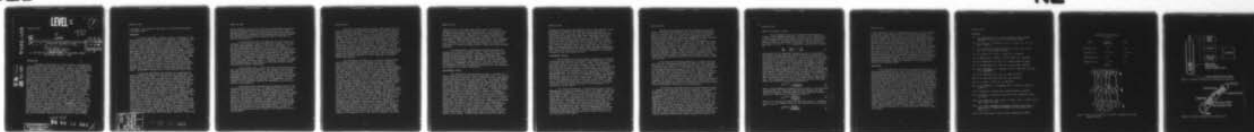
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ELECTRICAL CONDUCTIVITY OF SELECTED GRAPHITE INTERCALATION COMP--ETC(U)
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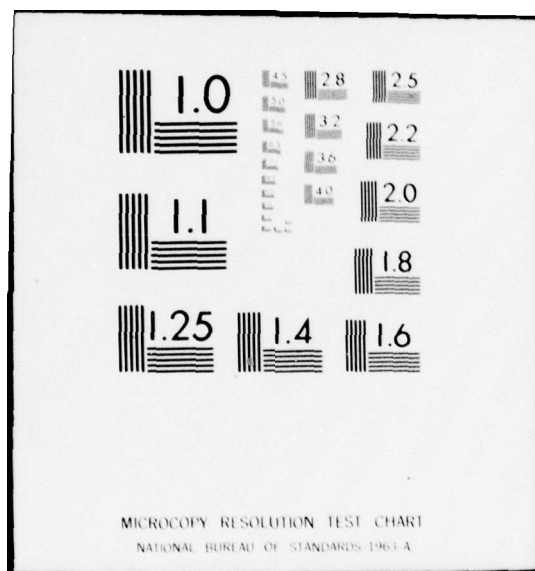
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ELECTRICAL CONDUCTIVITY OF SELECTED GRAPHITE INTERCALATION
COMPOUNDS IN THE RANGE $4K < T < 300K$

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INTRODUCTION

The Army's requirements for electric power in the field have increased dramatically in recent years as a result of increased use of special weapons, communications equipment, sensors, and other electric and electronic devices. The supply of the necessary power to the user is thus a matter of considerable importance to the Commander. At present the only systems available for transferring electrical power from source to user are wire and cable type systems. Rapid deployment and re-deployment capabilities, ease of handling and flexibility are essential characteristics of these systems for use in today's highly mobile tactical environment. The weight of presently available cable materials is a barrier to achieving these characteristics, especially for high power systems. Recent investigations have revealed a class of compounds, known as intercalated graphite, which appear promising as new conductor materials. Intercalation compounds are compounds of lamellar host materials which have atoms or molecules of a foreign chemical species inserted between layers. Graphite intercalation compounds are presently of interest in two major areas: in selective catalysis and as synthetic metals, especially for high infrared reflectance and high electrical conductivity. In particular, it has been shown that some of these materials exhibit higher electrical conductivity and have lower density than copper. These materials are of obvious interest to Army power programs. MERADCOM has initiated a cooperative effort with the University of Pennsylvania to investigate intercalated graphite compounds for possible application as an electrical conductor. MERADCOM's in-house program which supports this work is an investigation of the electrical conductivity of graphite and selected graphite compounds over the temperature range between

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4 and 300 K. The subject of this paper is an initial investigation of graphite fibers.

A detailed knowledge of graphite itself is necessary for any investigation of graphite intercalation compounds. Consequently, some of the properties of graphite will be reviewed briefly along with a discussion of recent investigations of graphite intercalation compounds. Graphite crystallizes into a layered structure consisting of planes of carbon atoms arranged in a hexagonal pattern. A model of the ideal crystal structure of graphite is shown in Figure 1. At room temperature the separation distance between nearest neighbor atoms in the basal planes is 1.415\AA , and successive basal planes are separated by 3.354\AA (1). The difference in separation distances is due to the two different types of bonds found in the graphite structure. Carbon atoms in the basal planes are linked together by covalent bonds; adjacent layers are weakly bonded to each other by van der Waals forces. The approximate two orders of magnitude difference between the two different bonds is reflected in its anisotropic physical properties, e.g., the measured value of Young's modulus which is 10^{13} dyne/cm² along the a-axis is thirty times greater than the c-axis value. Most graphite crystals have a layer stacking sequence ABAB....

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defects parallel to the a axis. Many early uncertainties observed in the electrical properties arising from varied sources and types of graphite available, as well as sample history, have been resolved with the development of techniques for stress-annealing pyrolytic graphite. This process provides near-ideal material which is comparable to natural crystals(2)(3).

It has been known since the 1860s that certain elements and compounds cause graphite to swell and increase in weight. Not until the 1930s were systematic studies of this effect undertaken. It is now well established that this effect is due to the formation of graphite intercalation compounds. Studies(4)(5) have shown that while the distance between the carbon layers is increased due to the intercalated atoms or molecules and the stacking order of the carbon layers is changed, there is almost no change in the in-plane separation of carbon atoms. Graphite intercalation compounds exist in various "stages" of intercalation. "Stage" is defined as the number of carbon layers separating intercalant layers. In general, graphite intercalation compounds possess a high degree of order with definite crystal structures and chemical compositions.

At the present time, at least 60 atomic and molecular species have been intercalated into graphite. Two classes of intercalation compounds have been identified. Intercalation with Group I elements from the Periodic Table (and some other metals) produces donor compounds(6)(7) while acceptor compounds are formed by intercalation with bromine(8), bisulfate(9), and strong acids(10). Many of the resulting intercalation compounds are metallic, or semimetallic in their behavior as the intercalant modifies the semimetallic electronic properties of the graphite.

Many intercalation compounds show an enhanced electrical conductivity along the a-axis (σ_a). The magnitude of this effect is controlled by the intercalation species and the stage of the resulting compound. The mechanism for the increased conductivity appears to be due to the transfer of fractional negative charge from the intercalated species to the carbon layers in a donor compound or from the carbon layers to the intercalated species in an acceptor compound. At the same time, the mobility, compared to graphite, is reduced due to enhanced electron-phonon scattering associated with the enlarged Fermi surface or an increase in the effective mass associated with changes in band structure or both of the preceding effects. In any event, the decrease in mobility is more than offset by the increase in carrier concentration, and the net effect is an increase in σ_a due to intercalation.

The effect of intercalation upon the c-axis conductivity (σ_c) is more complicated and illustrates a fundamental difference between donor and acceptor compounds. For donors, σ_c increases, and in some cases σ_c increases more than σ_a , e.g., for the first stage potassium compound KC_8 , $\sigma_a/\sigma_c = 34$, two orders of magnitude smaller than pure graphite. The essentially three dimensional behavior of the electrical conductivity in donor compounds is due primarily to the strong interaction between the electron clouds of the graphite structure and the valence electrons of the intercalants. For acceptors, σ_c drops significantly, and σ_a/σ_c increases strongly, by as much as 300 for arsenic pentafluoride (AsF_5) relative to pure graphite. It is concluded that acceptor compounds exhibit a two dimensional character due to the decreased attraction between carbon layers and weak interaction between intercalant and the graphite structure. This conclusion is supported by observed tendency of acceptor compounds to exfoliate during intercalation.

The significant increases in σ_a of acceptor compounds make them promising candidates for lightweight electrical conductors. Recent investigations of graphite intercalated with strong acid fluorides, antimony pentafluoride (SbF_5) and arsenic pentafluoride (AsF_5), have produced samples with electrical conductivities exceeding pure copper at room temperature. The first experiment demonstrating the high conductivity of acid fluorides was performed by Vogel(11) et al. on composite wires consisting of a graphite powder core intercalated with SbF_5 in a copper sheath. Results were obtained from a standard four terminal dc resistance method on samples 0.1cm dia. by 10cm long. The resistivity of the core was found to be $1.0 \times 10^{-6} \Omega \cdot cm$ or approximately two-thirds that of pure copper. Subsequent investigations on highly oriented pyrolytic graphite (HOPG) crystals intercalated with SbF_5 by Thompson(12) et al. and Fuzellier(13) et al. yielded resistivities five times greater than the composite wire results. These results are difficult to reconcile because the preparation of the samples was significantly different. The composite wires were fabricated in open air by compacting graphite- SbF_5 mixtures in copper tubes, heating overnight at $105^\circ C$, swaging the tubes to a fraction of their diameters, and then annealing. The HOPG samples were made with distilled materials and under moisture- and impurity-free conditions. In both cases, the SbF_5 conductivity results were obtained from dc resistance measurements, and are suspect due to the non-uniform distribution of current in the samples caused by the extremely high anisotropy of the acid fluoride samples. Zeller(14) et al. have developed a contactless radio frequency (r.f.) technique for measuring electrical conductivity in samples with large anisotropy. A sample is inserted into an induction coil with the c-axis parallel to the magnetic field. Eddy currents induced in the sample

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change the coil's inductance; this change causes a shift in the resonant frequency of an LC oscillator circuit. The conductivity of the sample is determined from a semi-empirical formula based on the resonant frequency shift. With the r.f. technique, Falardeau(15) et al. have measured conductivities (σ_a) exceeding silver at room temperature for HOPG crystals intercalated with AsF₅. The contactless r.f. technique eliminates the problem of non-uniform current density which can occur in four terminal dc measurements and is therefore well suited for measuring conductivities of highly anisotropic graphite compounds.

The investigation of intercalated graphite compounds has recently been extended to graphite fibers. These fibers are of considerable technological interest, and highly conducting fibers have obvious electrical applications. Vogel and his associates have recently produced graphite fibers intercalated with AsF₅ with room temperature resistivities from 200-500 $\mu\Omega \cdot \text{cm}$. The low temperature behavior of the electrical conductivity of the fiber samples is being investigated at MERADCOM. The temperature dependence of the electrical conductivity provides fundamental information about the mechanisms contributing to the overall conductivity.

EXPERIMENTAL DETAILS

The experimental apparatus shown in Figure 2 consists of a liquid helium cryostat with a variable temperature insert. The system permits the sample temperature to be controlled over the range between liquid helium temperature and room temperature. The graphite samples are mounted (Figure 3) on a sample block of OFHC copper which aids in maintaining uniform sample temperature; this sample holder also provides a heat sink for instrumentation leads and a mounting point adjacent to the sample for the temperature sensor. The sample temperature is monitored using a diode with a digital readout. Electrical conductivity measurements are made using a four terminal dc technique. A constant current source supplies sample currents of 10 microamperes, and the voltage drop across the sample is measured with a nanovoltmeter. Power dissipation is held to less than a microwatt to minimize spurious effects caused by self-heating of the sample. In a typical experiment, the sample is cooled to the lowest temperature and allowed to warm quasi-statically to room temperature. For convenience in taking data, the analog outputs of the nanovoltmeter and temperature monitor are connected to an X-Y recorder to produce a continuous record of each run. The four terminal dc measurement technique requires some care in its application and interpretation since anisotropic characteristics of graphite can lead to non-uniform current density in the sample. Graphite fiber samples which have length to

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thickness ratios greater than 1000 were used to assure uniform current distribution; individual filaments used in this experiment are nominally 8μ dia x 1 cm long. The work reported here was performed on Celanese GY-70 fibers with their high conductivity direction (a axis) oriented parallel to the fiber axis. Individual fibers are mounted on alundum wafers with platinum contacts baked on. Secure joints are made by soldering the fiber to these contacts with 80Au-20Sn solder paste and small pieces of platinum wire. The fibers were intercalated by immersing them in the intercalant, in the case of HNO_3 , or suspending them in AsF_5 vapor, under controlled temperature conditions. Observation of the fibers before and after intercalation with a microscope revealed that the fiber thicknesses were nominally unchanged by the intercalation process.

EXPERIMENTAL RESULTS

The reliability of the experimental apparatus was determined by measuring the temperature dependence of the resistivity of a piece of #36 AWG copper wire over the range 4.2-300K. The experimental data (open circles) are plotted in Figure 4 along with the Block-Grüneisen function (solid line) for simple metals. The semi-empirical Block-Grüneisen relation describes the ideal temperature dependence of the lattice or phonon contribution to the electrical resistivity at all temperatures. The relation gives the resistivity, ρ , $\propto T^5$ for $T < \theta$ (Debye Temp.) and $\rho \propto T$ for $T > \theta$, as required by theory. The agreement between the data and the theory is quite good indicating that the experimental apparatus provides reliable data. The systematic departure of the experimental data from the ideal theory is due to additional resistivity contributions, including faults due to annealing, impurities, and size effects especially at low temperatures, not accounted for in the theory.

The recent investigations of intercalated graphite fibers at MERADCOM have revealed two unexpected and not yet reported results in the temperature dependence of the electrical resistivity. First, for both pristine graphite fibers and the same fibers intercalated with either HNO_3 or AsF_5 , the resistivity increases monotonically with temperature from room temperature down to 4.2K, the boiling point of liquid helium at atmospheric pressure (low temperature limit of this investigation). In contrast, the basal plane resistivity(16) of natural and synthetic crystalline graphite decreases monotonically over the same temperature range. (This behavior of pristine HOPG graphite crystals has also been verified at MERADCOM as part of the experimental apparatus checkout.) Second, the dependence of fiber resistivity upon temperature is essentially linear, especially for the intercalated fiber samples.

The preceding results are clearly illustrated by plotting reduced resistivity ($\rho(T)/\rho(300K)$) data versus absolute temperature (K) for a pristine fiber and for the same fiber after intercalation. Figure 5 is such a plot for a fiber (F-1) intercalated with HNO_3 . Intercalation with HNO_3 was performed at MERADCOM with fibers supplied by the University of Pennsylvania. The resistivity of the fiber increased almost linearly to 140% of its room temperature value of $480\mu\Omega\cdot\text{cm}$ upon cooling to 4.2K. Intercalation with HNO_3 reduced the room temperature resistivity to $102\mu\Omega\cdot\text{cm}$ (almost a factor of 5 from the unintercalated value). The intercalated fiber's resistivity had a small, approximately linear temperature dependence (2% increase over the full temperature range). Several successive cyclings between 4.2K and room temperature reproduced the temperature dependence of the resistivity shown in Figure 5; changes in the absolute values of the resistivity were negligible indicating little de-intercalation of HNO_3 from the fiber.

Data obtained from another sample, Fig. 6, prepared from the same fiber and intercalated with HNO_3 confirmed the results obtained from sample F-1. Sample F-2 had nominally the same room temperature resistivity ($483\mu\Omega\cdot\text{cm}$) as F-1. The resistivity increased monotonically as the temperature was decreased to 4.2K; the resistivity at 4.2K was 136% larger than the room temperature value. Upon intercalation, the room temperature resistivity was reduced to $189\mu\Omega\cdot\text{cm}$ or approximately 40% of the unintercalated value. The resistivity of sample F-2 had a small, approximately linear temperature dependence (9% increase over the full temperature range), larger than the temperature dependence of sample F-1. Repeated temperature cyclings again verified the temperature dependence of the resistivity of the intercalated fiber with negligible effects due to de-intercalation.

Intercalation with AsF_5 produced the results shown in Figure 7. Samples intercalated with AsF_5 were supplied by the University of Pennsylvania, and consequently it was not convenient to measure resistivity before and after intercalating. The unintercalated curve is representative of data taken from other Celanese fiber samples at MERADCOM and is supplied only for qualitative comparison. The room temperature resistivity of the intercalated fiber was $241\mu\Omega\cdot\text{cm}$. The important result obtained by the AsF_5 intercalated fiber is that the temperature dependence of the resistivity was again linear over the range from 4K to room temperature. The magnitude of the change with resistivity of the AsF_5 intercalated fiber was larger (about 30%) than the magnitude of the change in the HNO_3 intercalated fibers (less than 10%). Again repeated cyclings between 4K and room temperature resulted in little change in the temperature dependence of the resistivity although de-intercalation caused measurable increases in the

absolute resistivity values.

The preceding results can be understood qualitatively in terms of a size dependence argument. When one or more dimensions of a sample becomes sufficiently small as in the case of a thin film or wire, collisions of the charge carriers with surfaces decrease the effective mean free path (mfp) of the sample. The effective mfp by Mathiessen's rule is the sum of independent components and is written as

$$\frac{1}{l_{eff}} = \frac{1}{l_{ph}(T)} + \frac{1}{l_{def}} \quad (1)$$

where $l_{ph}(T)$ is the temperature dependent mfp due to scattering of electrons by thermal vibrations (phonons) of the lattice and l_{def} is the temperature independent mfp due to scattering from defects. The term due to defects may be written as a sum of terms due to scattering from surfaces l_{sur} and scattering from impurities l_{imp} . It will be assumed that contribution due to impurities is negligible compared to the surface contribution. For sufficiently thin samples or at low temperatures where l_{ph} is very large due to negligible scattering from phonons, l_{eff} is approximately equal to l_{sur} . Microscopic examination of individual graphite fibers reveals that they are composed of large numbers of tangled fibriles whose thicknesses are probably no more than 1μ or about one-tenth the fiber thickness. If the effective mfp is limited by scattering at the fibrile surfaces or $l_{ph} \gg l_{sur}$, then the effective mean free path for a graphite fiber is equal to l_{sur} . The consequences of a size limited l_{eff} upon the fiber resistivity can be seen by writing the resistivity as:

$$\rho(T) = \frac{1}{n(T)e\bar{\mu}(T)} \quad (2)$$

where n is the temperature dependent carrier density, e the electronic charge and $\bar{\mu}(T)$ the temperature dependent mean mobility for both electrons and holes. The mean mobility can be represented approximately by a combination of relaxation processes as

$$\mu(T) = \frac{m^* v_F}{e l_{eff}(T)} \quad (3)$$

where m^* is the effective mass and v_F the Fermi velocity. Replacing l_{eff} by l_{sur} (for fibers) in Eq. (3), the resistivity can be written as

$$\rho(T) = \frac{m^* v_F}{n(T) e^2 l_{sur}} \quad (4)$$

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In this simplified model, the temperature dependence of the resistivity is due only to the change in carrier density with temperature. For crystalline graphite, $n(T)$ is found to decrease with temperature. This fact implies that $\rho(T)$ will increase as the temperature decreases for this model. The resistivity data for the unintercalated fibers exhibits this behavior and consequently supports this model. The data for the intercalated fibers does not present a uniform trend. The resistivity of the fibers intercalated with AsF_5 exhibit considerably greater temperature dependence, than the fibers intercalated with HNO_3 . The lack of temperature dependence of the resistivity can be accounted for in the size dependence model with a temperature independent carrier density. This is consistent with results obtained by Zeller(17) which supports a temperature independent carrier density in graphite intercalated with HNO_3 . The experimental data for the fiber intercalated with AsF_5 shows that the resistivity does depend upon temperature implying a temperature dependent carrier density based upon the size dependent model.

CONCLUSION

The investigation of intercalated graphite fibers has produced two interesting results, viz., the resistivity is a monotonically and approximately linearly decreasing function of the temperature for both pristine and HNO_3 - and AsF_5 -intercalated graphite fibers. These results have been interpreted in terms of a size dependence model in which the temperature dependence of the resistivity is essentially due to the carrier concentration. Further work which will include such additional parameters as the magnetoresistance are being undertaken to define more completely the mechanisms involved in the electrical transport properties. The results of these investigations will be used to further clarify the role of size effects and carrier concentration on the electrical conductivity of graphite fibers. Finally, to illustrate the possible technological application of these highly conductive intercalated graphite materials to the Army requirement for lightweight electrical conductors, Figure 8 shows a section of wire prepared by the group at the University of Pennsylvania. This conductor consists of a copper jacket with a core of SbF_5 -intercalated graphite; it was prepared by forming the intercalation compound in a sealed copper cylinder and swaging the cylinder to the desired diameter. The resistivity of the core was found to be approximately $1.0 \mu\Omega\cdot\text{cm}$ which corresponds to a conductivity about 70% greater than pure copper.

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COMPARISON OF GRAPHITE PROPERTIES
(T = 300 K)

PROPERTY	GRAPHITE (BASAL PLANE)	COPPER
MASS DENSITY (g/cc)	2.25	8.90
RESISTIVITY ($\Omega \cdot \text{cm}$)	40.0×10^{-6}	1.67×10^{-6}
CARRIER DENSITY (#/cc)	10^{19}	10^{23}
MOBILITY ($\text{cm}^2/\text{V} \cdot \text{SEC}$)	7×10^5	35

TABLE 1

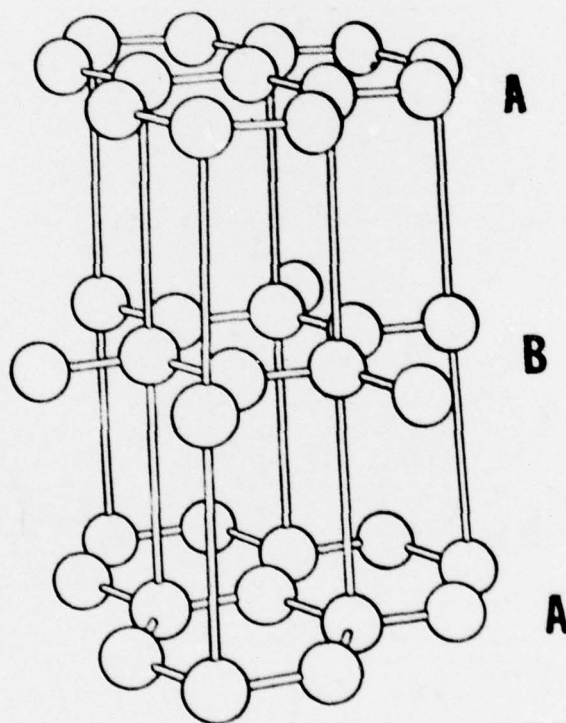


Figure 1. The crystal structure of graphite, showing the stacking sequence. ABAB....

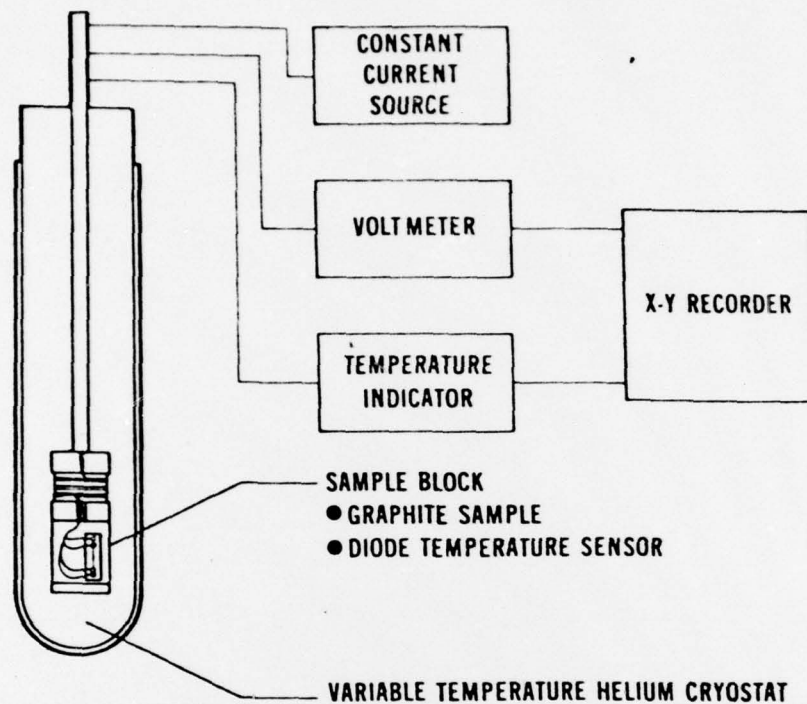


Figure 2. Schematic drawing of the experimental apparatus.

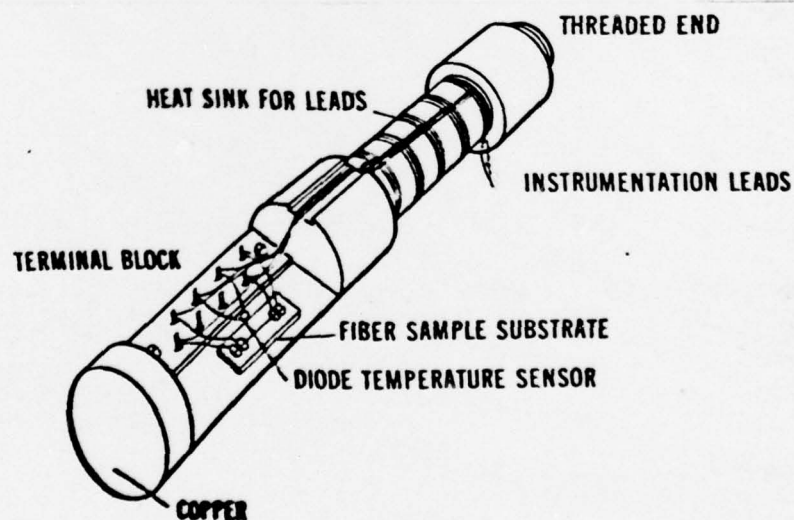


Figure 3. Artist's rendition of the sample block.

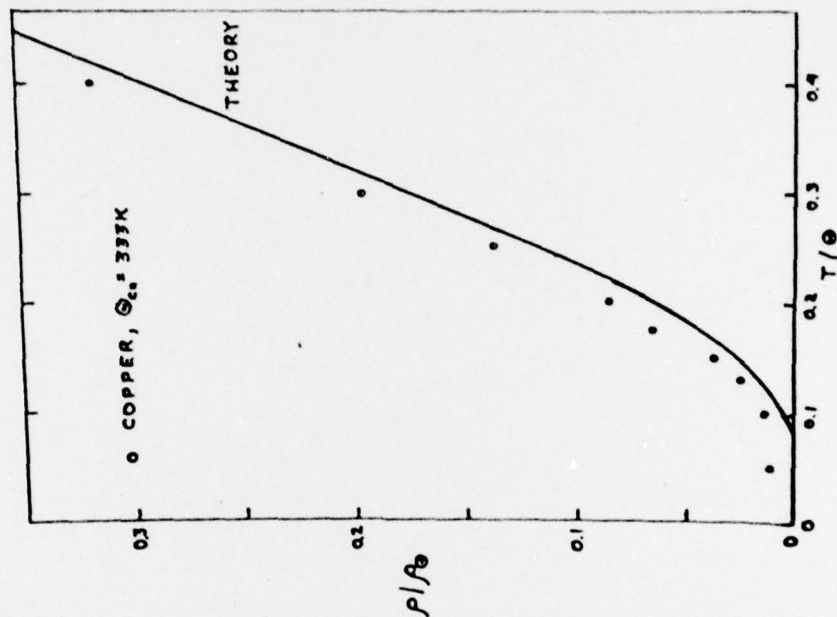


Figure 4. Resistivity versus temperature of a copper wire.

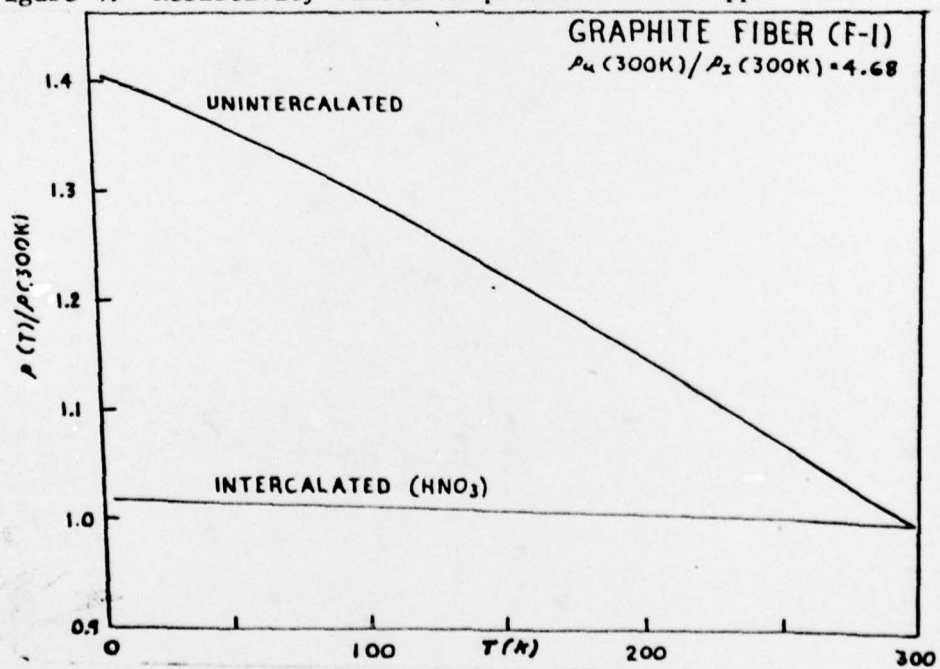


Figure 5. Resistivity versus temperature of graphite fiber (F-1).

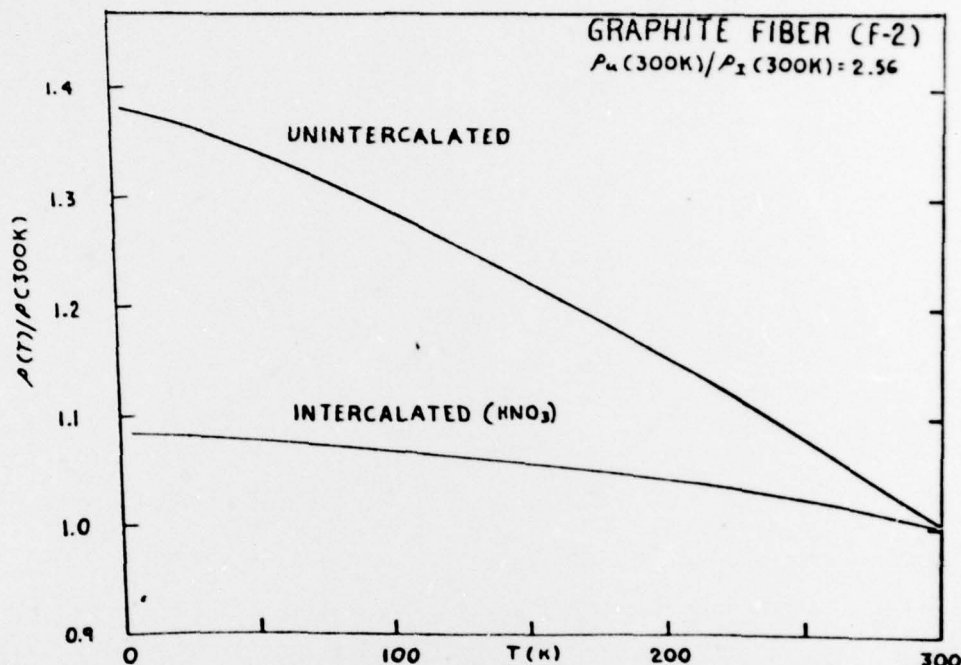


Figure 6. Resistivity versus temperature of graphite fiber (F-2).

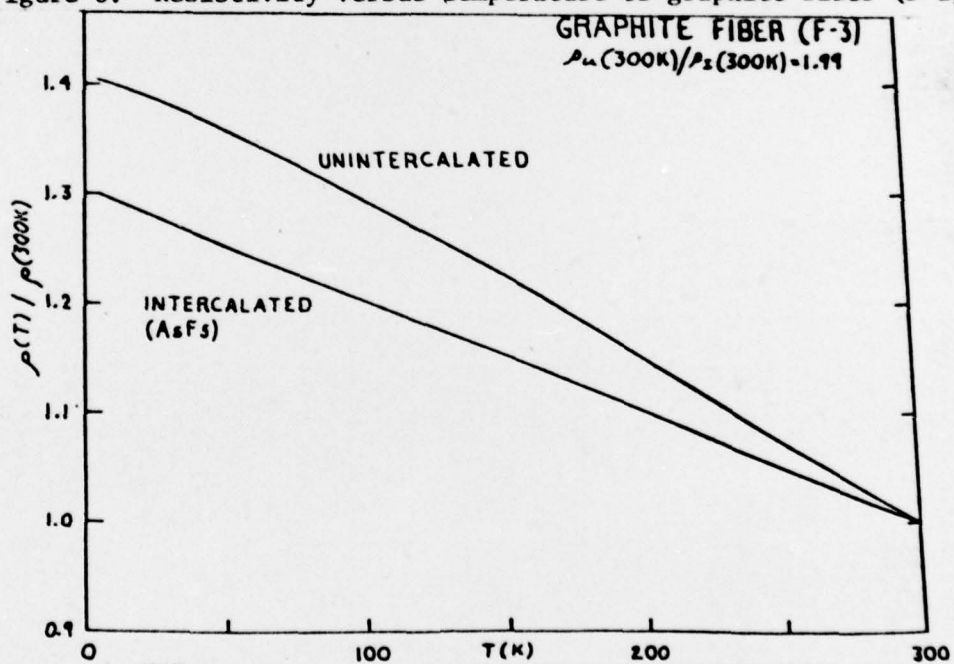


Figure 7. Resistivity versus temperature of graphite fiber (F-3).

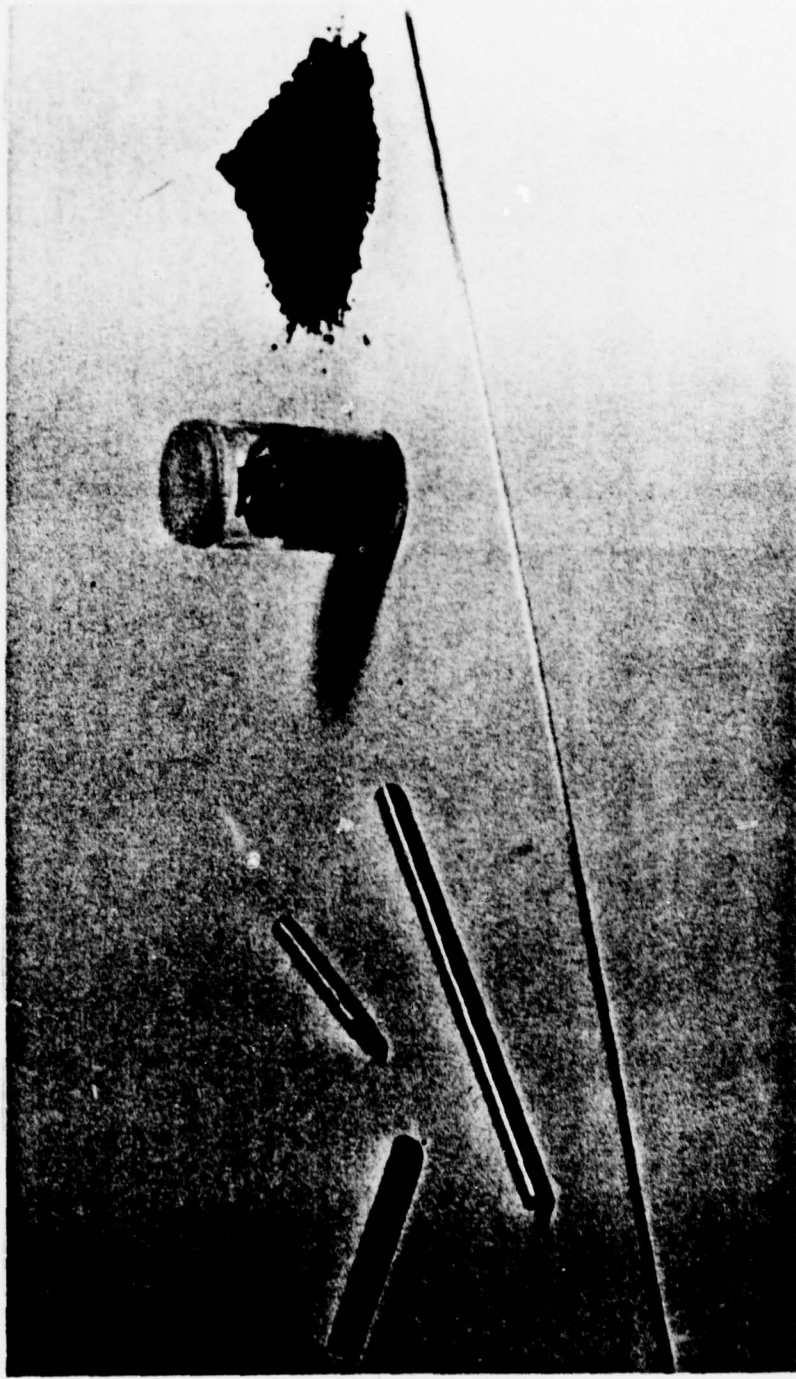


Figure 8. Photograph showing wire swaged from copper cylinder with an intercalated graphite core.